

THE ROLE OF OXYGEN FUNCTIONAL GROUPS IN THE MECHANISMS OF COAL LIQUEFACTION

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The hypothesis that the generation of soluble products in coal liquefaction is related to the cleavage of ether bridges or cross-links was proposed by Fisher et al. (1) and reiterated 20 years later by Takegami et al. (2). Recently, several workers have reported investigations on related topics, which include reductive alkylation (3,4), behavior of model compounds (5), and the distribution of oxygen-containing functional groups in liquefaction products (6). Nevertheless, the role of oxygen functionalities in coal liquefaction seems to us still to be obscure, and we therefore report here some attempts to clarify the matter. We have restricted our study to coal-tetralin interactions and relatively short contact times, in order to study phenomena in the early stages of the process.

EXPERIMENTAL

A high volatile bituminous coal having a low mineral matter content was chosen for the study (Table 1). Liquefaction runs were simulated in microreactors (~45 cc stainless steel tubes, with Swagelok fittings) charged with 5g of dried coal and 10 cc tetralin. Reactions were carried out at temperatures of 340 to 400°C and at contact times up to 30 minutes. Rapid heating of the contents was achieved by immersion of the vessels in a preheated fluidized sand bath; cooling was achieved by plunging the vessels into cold water. To ensure good mixing microreactors were vertically oscillated 450 times per minute with an amplitude of 1.25 cm. A more detailed description of the reactor assembly was given in (7). After reaction was completed, the contents were transferred to a 500 cc flask, diluted with hexane to a total volume of 500 cc, stirred and left for 24 hours to allow the precipitate (asphaltenes, preasphaltenes and residue) to be formed. To ensure that no change of sample properties occur during handling, such as oxidation or condensation of oxygen functional groups, a procedure was designed to avoid exposure to air, elevated temperatures or vacuum. The precipitate was filtered, washed with hexane and dried at room temperature in a stream of nitrogen for 24 hours. To correct analysis and extraction yields for adsorbed solvent, a portion of precipitate was dried in a vacuum ($<10^{-1}$ torr) at 100°C and the weight loss noted.

The following determinations were carried out on the hexane-insoluble precipitate. Figure 1 presents the procedure in block diagram.

1. Hydroxyl groups were determined by acetylation (8). The procedure was modified by using a larger excess of acetic anhydride.

2. Carbonyl groups were determined from the nitrogen uptake during reaction with hydroxylamine hydrochloride (9). We are aware that the amounts reported may not strictly correspond to carbonyl groups, but may include other functionalities. However, since carbonyl groups probably constitute the major part of the functionalities determined we will refer to all of them as carbonyls. This problem does not affect the conclusions expressed in a later part of this paper.

3. Benzene and pyridine solubilities were determined by exhaustive extraction under a nitrogen atmosphere in a Soxhlet apparatus.

4. High temperature ash was determined according to ASTM procedure D 271.

This value was used to calculate coal conversion to gases and hexane-solubles using the following equation derived from material balance considerations:

$$\% \left[\begin{array}{c} \text{hexane-solubles} \\ + \text{gases} \end{array} \right] = \frac{A_i - A_o}{A_o} \frac{10^4}{M_o} \quad 1)$$

where

A_i = ash content of precipitate

A_o = ash content of coal

M_o = mineral matter in coal.

5. Elementary analyses including direct oxygen were determined using a Perkin-Elmer Model 240 microanalyzer.

The loss of total oxygen was calculated from the difference between direct oxygen determinations and is reported per total initial oxygen in coal. The values will include a portion of the inorganic oxygen, estimated to be no more than 5-10% of the total oxygen; this error will presumably be the same for coal and insoluble reaction products.

A special sample of liquefied coal was prepared to investigate the effect of hydrogen bonding on benzene solubilities. Samples were prepared by reacting coal with tetralin at 400°C for 10 minutes, and then following the above described procedure to obtain the hexane-insoluble precipitate.

We were able to introduce different quantities of trimethylsilyl groups on to the hydroxyl groups by varying the reflux time of 2g of sample in 40 cc tetrahydrofuran and 10 cc hexamethyldisilazane. After reaction, the contents were diluted with hexane, filtered and the residue was washed with hexane. Because some hexane-soluble materials were generated by the above procedure, the filtrate was collected and solvent plus unreacted hexamethyldisilazane removed by distillation, after which the undistilled material was weighed. The number of hydroxyl groups blocked was estimated from the change in H/C atomic ratios between a blank run (sample + THF), and the products of silylation (residue + dry solid from filtrate).

Differences in solubilities between blank and blocked samples are reported as the increase of benzene solubilities.

RESULTS AND DISCUSSION

Yields of pyridine-solubles, benzene-solubles and hexane-solubles plus gases are plotted *versus* the loss of oxygen for various contact times and temperatures in Figures 2a-d. There appear to be correlations between the various sets of data, from which it is tempting to draw mechanistic conclusions. Thus, as already noted, Fisher et al. (1) used a similar correlation to that in Figure 2a, between conversion to benzene-soluble products and loss of total oxygen content, to infer that splitting of ethers was a rate-determining step. But other correlations found here (Figures 2b and 2c) could support alternative hypotheses, such as that the elimination of hydrogen-bonding between hydroxyl groups is crucial to liquefaction. In any case, there is a correlation between loss of total oxygen and oxygen as OH (Figure 3). Thus we believe that in coal liquefaction, where a number of processes are undoubtedly occurring concurrently, unambiguous conclusions about mechanisms cannot be drawn directly from correlations such as those illustrated in Figures 2a-d. Nevertheless, we believe that useful conclusions can be drawn from the data, though in a less direct way.

In examining the magnitude of changes of the oxygen functionalities during generation of pyridine-soluble materials, we have observed that the major loss of

oxygen occurred with the so-called unaccounted oxygen (unaccounted = total - hydroxyl - carbonyl) and very little change was detected in the contents of hydroxyl and carbonyl groups at these stages of liquefaction (Figure 4). If we presume that the unaccounted oxygen is comprised primarily of the ether oxygen, then Figure 4 strongly suggests an important contribution of these functionalities to generation of pyridine-soluble materials. Although we cannot estimate an exact amount of the ether oxygen being cleaved, we can, however, estimate the maximum amount of the ether oxygen linkages being cleaved per 100 initial carbon atoms in coal. From a material balance we can show that:

$$\left[\begin{array}{c} \text{amount of ether} \\ \text{oxygen cleaved} \end{array} \right] \leq \left[\begin{array}{c} \text{total oxygen} \\ \text{loss} \end{array} \right] - \left[\begin{array}{c} \text{hydroxyl + carbonyl} \\ \text{oxygen loss} \end{array} \right] \quad 2)$$

making the reasonable assumption that the amount of oxygen in the hexane-solubles is insignificant. Figure 5 shows the right side of the above inequality *versus* generation of pyridine-soluble materials plus gases (conversion of coal). The regression equation for the line is:

$$y = -0.230 + 0.0336x \quad 3)$$

The second coefficient (slope) has a standard deviation $\sigma = 0.0030$. The amount of ether oxygen linkages, ϕ , being cleaved per 100 initial carbon atoms was calculated from the slope using the equation:

$$\phi = \left(\frac{12}{16} \right) \times \left(\frac{10^4}{\% C} \right) \times (\text{slope}) \quad 4)$$

where $\% C$ = percent carbon in coal, dmmf.

Substituting $\% C = 83.47$, slope = 0.0336

gives $\phi = 3.0 \pm 0.3$

This number is slightly larger than the amount estimated by Ignasiak et al. (4) in their study of products from reductive alkylation of a high-rank vitrinite, i.e., two ether linkages cleaved per 100 original C atoms. The difference in rank of vitrinites could explain the discrepancy. The question arises, is ether cleavage, in the amount indicated, sufficient to generate the observed yields of pyridine-soluble materials, or does the ether cleavage have only a contributing role, like that discussed below for the effect of hydrogenolysis of hydroxyl groups on generation of benzene-soluble materials.

It should be noted that the plot in Figure 5 is purely empirical. The points represent data obtained in runs at different temperatures and reaction times, so it is somewhat surprising that they lead to a linear regression of high significance. One possible inference from the finding is that the coal behaves in a manner characteristic of a uniformly cross-linked polymer.

We have conjectured from Figure 2c that since hydrogenolysis of hydroxyl groups cannot result in substantial lowering of the molecular weight, the effects observed are due to elimination of hydrogen bonding by removal of the hydroxyl groups. If this is true, then by replacing the hydroxyl hydrogen with a substituent like trimethylsilyl, we should decrease the number of hydrogen bonds and increase the benzene solubility. The results of the treatment with hexamethyldisilazane are shown in Figure 6. A marked increase of benzene solubility suggests that, during liquefaction, hydrogenolysis of hydroxyl groups can play an important role in the generation of benzene-soluble materials. (By extrapolation, the results indicate that over 80% of the total pyridine-soluble material could become benzene-soluble). However, if

we compare the rate (slope) of generation of benzene solubles when hydroxyl groups are blocked to the rate (slope) when hydroxyl groups are removed during liquefaction (dashed line, predicted from Figure 2c by correcting for yield of gases), we must concede that hydrogenolysis of hydroxyl groups during liquefaction cannot account for more than 40% of the benzene-soluble materials generated. The remainder, presumably, is generated via different mechanistic routes.

Suppose it should prove possible to make hydrogenolysis of hydroxyl groups more competitive by introducing selective catalysts. Would we gain anything from such a modification of the liquefaction process? In terms of hydrogen consumption the answer seems to be, yes. To produce more benzene solubles merely by hydrogenolysis of OH groups, we would have to add about 0.8% of hydrogen (w/w of pyridine-soluble materials). On the other hand, Whitehurst et al. (5) give 2.2% for the actual hydrogen consumption in the hydrogenolysis of asphaltols from a similar coal to benzene solubles under SRC liquefaction conditions.

In view of the large amount of experimental work involved, we have only studied one coal. One principal finding is that "unaccounted" oxygen, mostly ether, is removed much more rapidly in the early stages of liquefaction than other oxygen-containing groups, and a maximum amount of ether groups split has been estimated. It has been shown that hydrogenolysis of OH groups has an important effect on the solubility of liquefaction products. The quantitative, or semi-quantitative, aspects of these conclusions probably will not apply to other coals, but it seems likely that the qualitative identification of important phenomena will be relevant generally.

SUMMARY

A number of processes taking place during liquefaction are concurrent and, therefore, no mechanistic inferences can be made from simple relationships between generation of different classes of soluble materials and loss of coal functionalities, such as oxygen functional groups.

The amounts of ether oxygen being cleaved during the process are not larger than 3.0 ± 0.3 ether oxygen linkages per 100 initial carbon atoms in the coal studied, and loss of "unaccounted" oxygen, assumed to be principally ether, increases linearly with conversion, as measured by pyridine solubility.

Blocking of hydroxyl oxygen with trimethylsilyl groups results in an increase in the benzene solubilities of pyridine-soluble materials. However, comparison of the rates of increase when hydroxyl groups are blocked with the rates when hydroxyl groups are removed during liquefaction leads to the inference that during liquefaction no more than 40% of benzene-soluble materials are generated from benzene-insoluble, pyridine-soluble materials by the mechanism of hydrogenolysis of oxygen functional groups.

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TABLE 1
Elemental Analysis, PSOC-330, Middle Kittanning Seam, Pa.
all data on dry mineral-containing basis

Mineral Matter	7.96%	Oxygen (direct)	9.03%*
Carbon	76.83%	Hydroxyl oxygen	3.8%
Hydrogen	4.97%	Carbonyl oxygen	1.2%
Nitrogen	1.71%	Vitrinite content	71.4%
Sulphur (organic)	0.67%	Pyridine solubility	13.2%
Oxygen (by difference)	7.86%	Pyritic sulphur	2.08%

*not corrected for interferences by mineral matter.

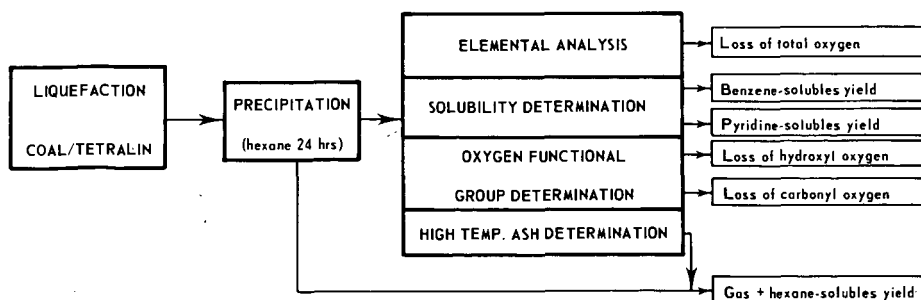


Fig. 1 PROCEDURE BLOCK DIAGRAM

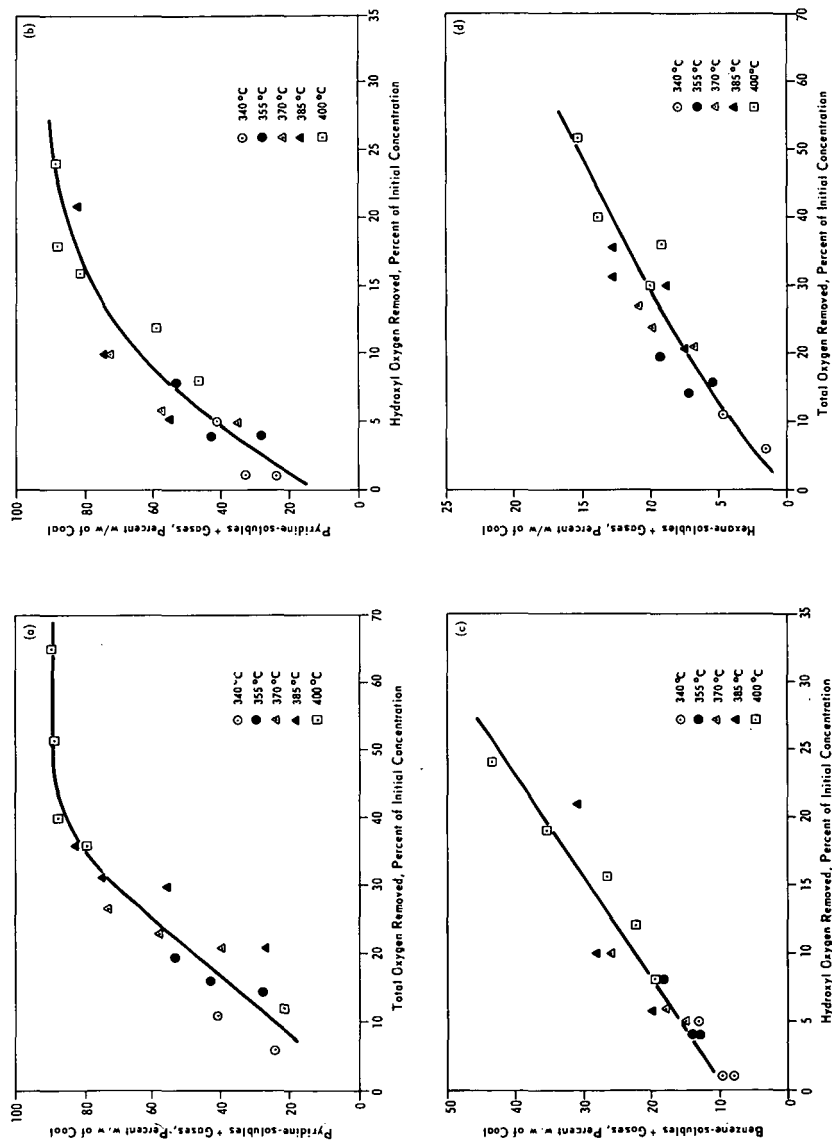


Fig. 2 RELATIONSHIPS BETWEEN GENERATION OF (a) PYRIDINE-SOLUBLE MATTER AND LOSS OF TOTAL OXYGEN, (b) PYRIDINE-SOLUBLE MATTER AND LOSS OF HYDROXYL OXYGEN, (c) BENZENE-SOLUBLE MATTER AND LOSS OF TOTAL OXYGEN, (d) HEXANE-SOLUBLE MATTER + GASES AND LOSS OF TOTAL OXYGEN, ALL ON DRY COAL BASIS

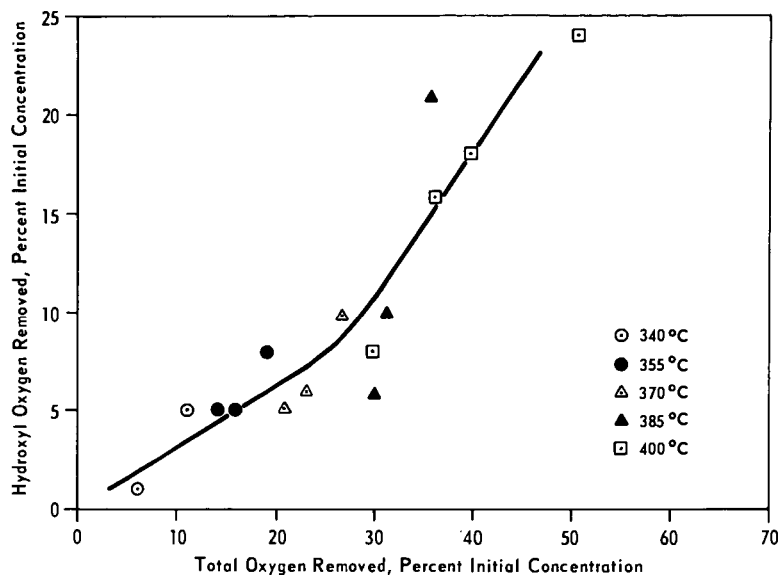


Fig. 3 RELATIONSHIP BETWEEN LOSS OF HYDROXYL OXYGEN AND TOTAL OXYGEN

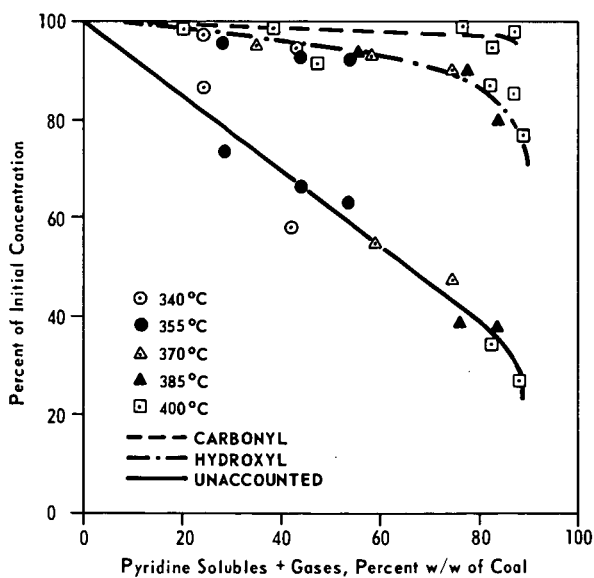


Fig. 4 LOSS OF OXYGEN FUNCTIONAL GROUPS VS GENERATION OF PYRIDINE SOLUBLE MATTER, DRY COAL BASIS

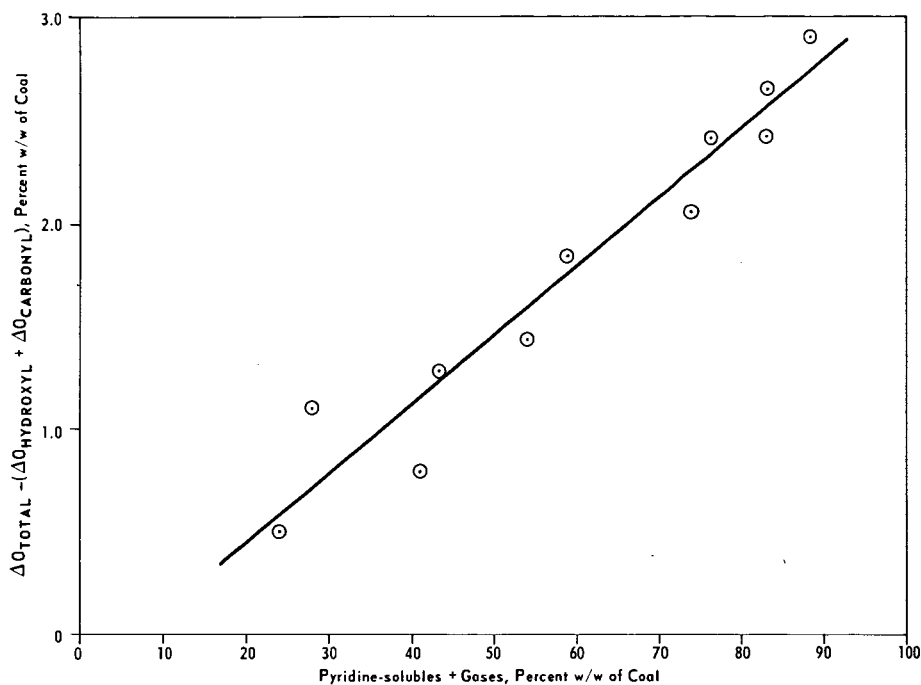


Fig. 5 RELATIONSHIP BETWEEN MAXIMUM ETHER OXYGEN CLEAVED AND GENERATION OF PYRIDINE SOLUBLES + GASES, PERCENT W/W OF COAL

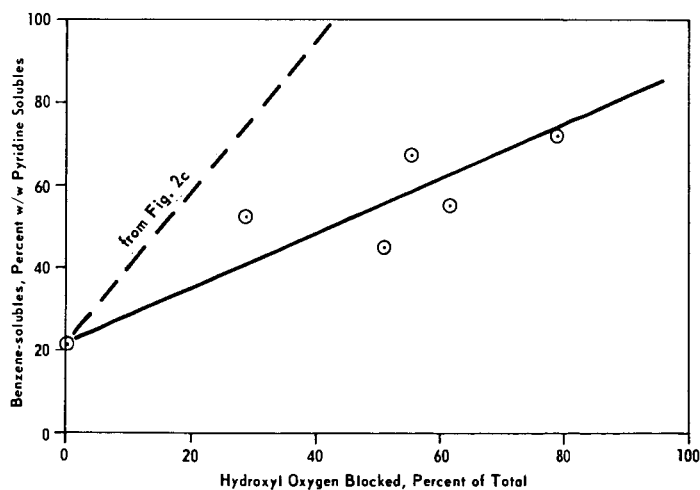


Fig. 6 EFFECT OF HYDROXYL HYDROGEN SUBSTITUTION ON BENZENE SOLUBILITIES